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Photoelectron Spectroscopy of the *o*-, *m*-, and *p*-Methylbenzyl Radicals. Implications for the Thermochemistry of the Radicals and Ions

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Abstract: The first photoelectron bands of *o*-, *m*-, and *p*-methylbenzyl radicals have been obtained by studying the products from the flash vacuum pyrolysis of the appropriate alkyl nitrites. The photoelectron spectra all show vibrational structure, and the vertical and adiabatic ionization potentials coincide in all cases. The ionization potentials are 7.07 ± 0.02, 7.12 ± 0.02, and 6.96 ± 0.02 eV for the *o*-, *m*-, and *p*-methylbenzyl radicals, respectively. These values are all lower than the adiabatic ionization potential of the benzyl radical (7.20 ± 0.02 eV). These results, when combined with relative heterolytic bond energy data, give accurate relative homolytic bond-dissociation energies. The homolytic benzylic C–H bond-dissociation energies in *o*-, *m*-, and *p*-xylene were found to be 0.91 ± 0.5, 0.36 ± 0.5, and 0.58 ± 0.5 kcal mol^{-1} lower than the benzyl C–H bond energy in toluene, respectively. The implications of these ionization potentials and relative bond energies for the absolute values of the heterolytic and homolytic benzyl C–H bonds in toluene and the tertiary C–H bond in isobutane are discussed.

Homolytic bond-dissociation energies have previously been measured by kinetic techniques such as bromination[1] and iodination[2] kinetics and very low pressure pyrolysis (VLPP).[3] These techniques all measure individual absolute homolytic bond energies and are subject to moderate uncertainty. Difficulties also arise from complications such as chain and wall reactions.[2] As an alternative to these experiments we have recently explored the combination of relative heterolytic bond-dissociation energies, i.e., relative hydride and chloride affinities from high-pressure mass spectrometry, with ionization potentials of radicals from photoelectron spectroscopy to provide highly precise *relative* homolytic bond-dissociation energies.[4] The relationships between relative heterolytic bond-dissociation energies, ionization potentials, and relative homolytic bond-dissociation energies are shown in the thermochemical cycle in Figure 1, where X = H or Cl. The difference in the adiabatic ionization potentials for two radicals, ΔH° for reaction 1, can be combined with the difference in heterolytic bond energies for the corresponding carbonium ions, ΔH° for reaction 2, to yield the difference in homolytic bond-dissociation energies, ΔH° for reaction 3. Errors associated with

$$R_1^+ + R_2^\cdot \rightarrow R_2^+ + R_1^\cdot \qquad (1)$$

$$R_1X + R_2^+ \rightarrow R_2X + R_1^+ \qquad (2)$$

$$R_1X + R_2^\cdot \rightarrow R_2X + R_1^\cdot \qquad (3)$$

the ionization potential measurements are about 0.4 kcal mol^{-1}, and the relative heterolytic bond dissociation energy measurements have errors of about 0.2–0.4 kcal mol^{-1}.[5] Hence relative homolytic bond energies can be determined to within an accuracy of about 0.4–1.0 kcal/mol^{-1} with this method, which approaches the accuracy of the best kinetic methods.[2] The precise relative homolytic bond energies obtained in this way can be used to check the consistency of the bond energies obtained by kinetic methods and to extend bond energy measurements to include values that have not been previously determined by kinetic methods.

In this study the first photoelectron bands and adiabatic ionization potentials of the *o*-, *m*-, and *p*-methylbenzyl radicals have been obtained. The first photoelectron band of the unsubstituted benzyl radical is available from a previous study from this laboratory.[6] The methyl-substituted benzyl radicals make an excellent test case for this method of determining bond energies. The effect of substituents on the benzyl bond energies and reactivity of substituted toluenes has been the subject of extensive study.[7] Several recent studies have shown the importance of benzyl C–H bond energy changes caused by substitution in determining H atom abstraction rates from substituted toluenes.[8] The benzyl C–H bond energy in toluene is used as a reference for other homolytic bond energy determinations, and there is a need for further experimental work to confirm and refine the kinetic values for this bond energy.[9]

The earliest measurements of the benzylic C–H bond energies in toluene and substituted toluenes were made by Szwarc and co-workers, who studied the kinetics of C–H bond fission in toluene and the three xylenes.[10] They determined benzylic C–H bond energies of 77.5 kcal mol^{-1} for toluene and 74.0, 77.5, and 75 kcal mol^{-1} for *o*-, *m*-, and *p*-xylene, respectively. A subsequent study of gas-phase free radical bromination kinetics yielded a value of 89.6 kcal mol^{-1} for the benzyl C–H bond energy in toluene.[1] Benson critically reviewed much of the early kinetic work on toluene and the xylenes and recommended 88.3 kcal mol^{-1} for the benzyl C–H bond energy in toluene.[11] Zavitsas recommended a value of 88.1 kcal mol^{-1},[12] and Golden gave a value of 88.0 ± 1 kcal mol^{-1} in a recent review.[9] Further support for $DH^\circ(C_6H_5CH_2\text{–}H)$ = 88 ± 1 kcal mol^{-1} comes from a recent proton affinity study by Meot-Ner which yielded a value of 88.9 kcal mol^{-1}.[13] A recent VLPP study of benzyl C–C bond strengths in substituted ethylbenzenes yielded 74.1 ± 0.6 kcal mol^{-1} for the benzylic C–C bond in ethylbenzene.[3] The same study yielded values of 72.9 ± 0.6, 73.8 ± 0.5, and 73.7 ± 0.5 kcal mol^{-1} for the benzylic C–C bond energies in *o*-, *m*-, and *p*-methylethylbenzene, respectively, thus suggesting that methyl substitution has a very small effect on the benzyl bond energy in toluene.

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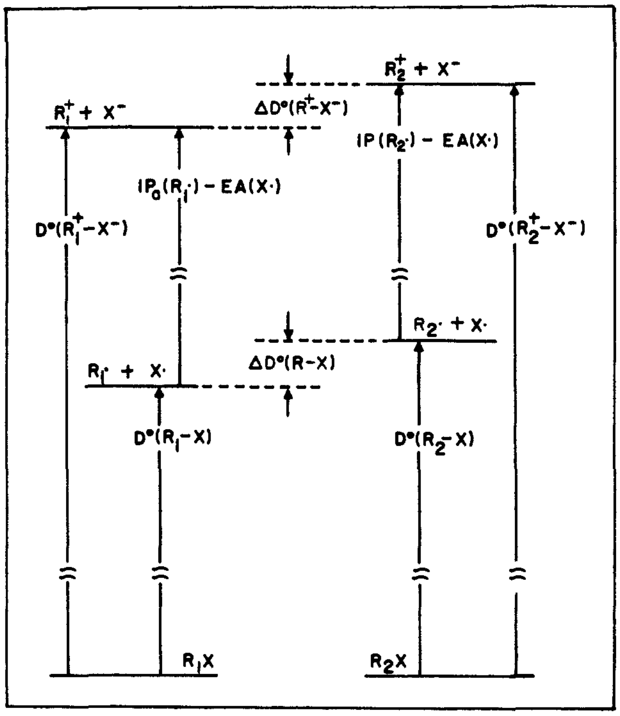

Figure 1. Thermochemical scheme showing the relationships between relative homolytic bond energies, $\Delta D°(R-X)$, relative heterolytic bond energies, $\Delta D°(R^+-X^-)$, and free radical adiabatic ionization potentials, IP ($R^\cdot$). For comparison of the two species R_1X and R_2X, heats of formation of the parent molecules are used to define the zero of the energy scales.

Experimental Section

The radicals studied in this work were produced by pyrolysis of the appropriate alkyl nitrites, (reactions 4 and 5). The nitrites were synthesized from *o*-, *m*-, and *p*-methylphenethyl alcohol obtained from Aldrich, using a standard method.[14] In each case the purity of the nitrite product was checked by NMR spectroscopy.

$$RCH_2ONO \rightarrow RCH_2O^\cdot + NO \qquad (4)$$

$$RCH_2O^\cdot \rightarrow R^\cdot + CH_2O \qquad (5)$$

The photoelectron spectrometer used in these experiments was an instrument of standard design that has been modified to study the products of flash vacuum pyrolyses. A description of the instrument can be found in a previous publication.[6] The pyrolyzer used in this study was 2 cm in length, corresponding to the "long" pyrolyzer used in an earlier study.[15]

Photoelectron spectra of the pyrolysis products were obtained with He I radiation, at temperatures from 450 to 650 °C. The energy scales for the pyrolysis product spectra were calibrated with He Iα bands of CH_3I and CH_2O and the He Iβ bands of CH_3I. The room temperature spectra of the nitrites were calibrated with the He Iα bands of Ar and CH_3I. The typical instrumental resolution for these experments was 30–35 mV, as determined from the fwhm of the $Ar\,^2P_{3/2}$ band. The instrumental resolution is the full-width at half-maximum of an atomic line. Peak maxima can easily and reproducibly be determined to within 0.02 eV with careful calibration in cases where the peak is sharp. Error limits of 0.03–0.05 eV are assigned for cases where the peak maxima are difficult to locate or calibrate accurately.

Results

The He I photoelectron spectra of the *o*-, *m*-, and *p*-methylphenethyl nitrites are similar to the spectrum of the 2-phenylethyl nitrite obtained in a previous study,[6] and the spectra are not reproduced here. The vertical ionization potentials of the first photoelectron bands of *o*-, *m*-, and *p*-methylphenethyl nitrite are 8.88 ± 0.05, 8.92 ± 0.05, and 8.58 ± 0.05 eV, respectively. The spectra of the first photoelectron bands of *o*-, *m*-, and *p*-methylbenzyl radicals are shown in Figure 2 along with the spectrum of benzyl radical from the previous study.[6] The spectra shown in Figure 2 were recorded at a pyrolyzer temperature of 570 °C, which was sufficient to decompose all of the nitrite. The spectra shown in Figure 2 appeared at pyrolysis temperatures above 380 °C and were independent of temperature over the range studied, to 650 °C.

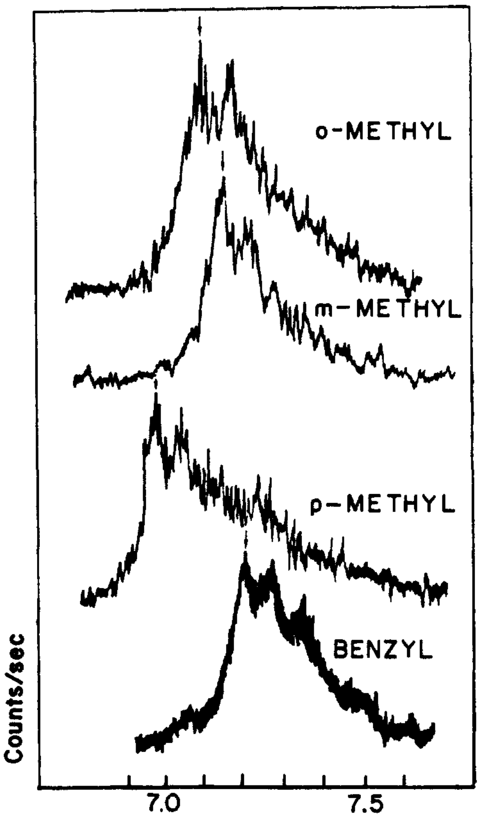

Figure 2. The He I photoelectron spectra of benzyl radical (ref 6) and the methyl-substituted benzyl radicals (this work). The radicals were produced by pyrolysis of the appropriate alkyl nitrites at 570 °C. The adiabatic ionization potentials are indicated by the arrow on each spectrum.

As is the case for the benzyl radical, all of the methylbenzyl radicals show evidence for vibrational structure in the first band of their photoelectron spectra. The spectra are all similar, and the adiabatic and vertical ionization potentials coincide in all cases. From the spectra in Figure 2 the adiabatic ionization potentials are 7.07 ± 0.02 eV, 7.12 ± 0.02 eV, and 6.96 ± 0.02 eV for the *o*-, *m*-, and *p*-methylbenzyl radicals, respectively. The vibrational structure in the methylbenzyl radicals is less well resolved than in the benzyl radical, and the vibrational spacings can only be determined within an error of 80 cm^{-1}. The vibrational frequencies observed are 480, 490, and 400 cm^{-1} for the *o*-, *m*-, and *p*-methylbenzyl radicals, respectively. The vibrational frequency observed in the first band of the benzyl radical photoelectron spectrum is 560 cm^{-1}.[6]

Discussion

The band shapes and vibrational envelopes of the first photoelectron bands of the *o*-, *m*-, and *p*-methylbenzyl radicals are all similar to each other and to the benzyl radical.[6] However, the radicals have significantly different ionization potentials, which suggests that photoelectron spectroscopy could be used as a technique to distinguish the isomeric xylyl radicals.

The ionization potentials of benzyl[6] and *m*- and *p*-methybenzyl radicals obtained by PES are considerably lower than those reported by Lossing in an earlier electron-impact study.[16] His

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Table I. Heterolytic and Homolytic Bond Energies for Isobutane, Toluene, and the Isomeric Xylenes[a]

R	IP	$\Delta H_f°[R^+]$	DH°[R–H]	$D°[R^+–H^-]$	$\Delta H_f°[R^•]$
tert-butyl	(6.70)[b]	(166.5)[c]	96.5	233.7	12.0
$C_6H_5CH_2$	(7.20)[d]	214.1[e]	88.2	236.9	48.1
o-$CH_3C_6H_4CH_2$	(7.07)[f]	202.8[g]	87.3	233.0	39.8
m-CH_3-$C_6H_4CH_2$	(7.12)[f]	204.0[g]	87.8	234.7	39.8
p-$CH_3C_6H_4CH_2$	(6.96)[f]	200.3[g]	87.6	230.8	39.8

[a] All values are in kcal mol^{-1} except the IP which are given in eV. Values in parentheses are numbers measureed in this work or other studies. *All* other values are derived from the numbers in parentheses and relative hydride and chloride affinities from ref 5. Errors on all quantities are estimated to be ±1 kcal mol^{-1}, but relative bond energies and hydride affinities are known to ±0.5 kcal mol^{-1} for toluene and the xylyl radicals (see text). All calculations use the convention that the heat of formation of an electron at rest is zero at all temperatures.[24] [b] Reference 20. [c] Recommended value, see ref 19. [d] Reference 6. [e] Derived by using the relative chloride affinity between $(CH_3)_3C^+$ and $C_6H_5CH_2^+$ from ref 5. $\Delta H_f°[(CH_3)_3CCl]$ and $\Delta H_f°[C_6H_5CH_2Cl]$ from ref 22, $\Delta H_f°[Cl^•]$ from ref 23, the IP of $C_6H_5CH_2$ from column 1, and $\Delta H_f°[(CH_3)_3C^+]$ from column 2, row 1. [f] This work. [g] From $D°[R^+–H^-]$, $\Delta H_f°[H^-] = 34.8$ kcal mol^{-1}, ref 19b, and the hydrocarbon heats of formation, ref 22.

measurements yielded adiabatic ionization potentials of 7.73 ± 0.08, 7.65 ± 0.03, and 7.46 ± 0.03 eV for benzyl radical and *m*- and *p*-methylbenzyl radicals, respectively. In a later electron impact study of the benzyl radical Lossing obtained a vertical ionization potential of 7.27 ± 0.03 eV,[17] which is in better agreement with the PES result of 7.20 ± 0.02 eV.[7] Lossing attributed the difference between the two electron-impact results to an underestimation of the onset of the ionization efficiency curve in the earlier study. This may also explain the difference between the electron impact and PES results for the *m*- and *p*-methylbenzyl radicals.

Relative Bond Energies and Reactivities. The bond-dissociation energies of the benzyl C–H bonds, relative to the benzyl C–H bond in toluene ($\Delta H°$ for reaction 3), were calculated from measured enthalpy changes for reactions 1 and 2 as described in the introduction. Kebarle and co-workers determined the relative chloride affinities of the benzyl and the *o*-, *m*-, and *p*-methylbenzyl cations in a high-pressure mass spectrometry equilibrium study which provided values with error limits of 0.2 kcal mol^{-1} and good internal consistency.[5] The heats of formation of the parent xylyl chlorides have not been determined, so it is not possible to convert the relative chloride affinities to relative hydride affinities. Equality of the relative chloride and hydride affinities of two cations, R_1^+ and R_2^+, requires that eq 6 be satisfied. For similar compounds like benzyl chloride and the xylyl chlorides, this

$$\Delta H_f°(R_1H) - \Delta H_f°(R_2H) = \Delta H_f°(R_1Cl) - \Delta H_f°(R_2Cl) \quad (6)$$

condition would be expected to be met, and the chloride and hydride affinities would be expected to be nearly equal.[5] Evidence to support the equality of the hydride and chloride affinities in this case comes from a theoretical calculation of the hydride affinities,[18] which gave values for the relative hydride affinities of *p*-, and *m*-methylbenzyl cations that are very close to the relative chloride affinities determined by Kebarle and co-workers.[5] With the assumption that the relative hydride and chloride affinities are equal, the homolytic benzyl C–H bond-dissociation energy of the ortho species was found to be 0.9 ± 0.5 kcal mol^{-1} lower than that for toluene, while the bond energies for the meta and para species were 0.36 ± 0.5 kcal mol^{-1} and 0.59 ± 0.5 kcal mol^{-1} lower, respectively, than that for toluene. These results agree qualitatively with the earlier work by Szwarc,[10] who found that the bond energies in *o*-, *m*-, and *p*-xylene were 3.5, 0.0, and 0.5 kcal mol^{-1} lower than the C–H bond energy in toluene. Our results show better quantitative agreement with a more recent VLPP study on the benzylic C–C bond energies in substituted ethylbenzenes,[3] which showed that the benzylic C–C bond energies in *o*-, *m*-, and *p*-methylethylbenzene are 1.20, 0.31, and 0.41 kcal mol^{-1} less than the benzylic C–C bond energy in ethylbenzene. Benson has reexamined the early work of Szwarc and others and concluded that many of the experiments suffer from errors due to chain reactions and wall reactions.[11] The results from our laboratory and the VLPP results suggest that methyl substitution at the meta and para positions has only a small effect on the benzyl bond energy in toluene. The larger effect of methyl substitution at the ortho position is probably due to steric considerations, as has been suggested by Barton and Stein.[3] The small but significant effect on benzylic C–H bond energies caused by methyl substitution at the meta and para positions in toluene could be partly responsible for the different rates observed for H atom abstractions from *m*- and *p*-xylene.[7]

Absolute Bond Energies. In order to assign absolute bond energy values to the xylenes studied in this work, it is necessary to choose a reference absolute bond energy or hydride affinity. The most recent recommended value for $\Delta H_f°[(CH_3)_3C^+]$ is 166.5 kcal mol^{-1},[19] from which the hydride affinity of the *tert*-butylcarbonium ion can easily be derived. Using this value for the heat of formation of the *tert*-butylcarbonium ion with the adiabatic ionization potential of the *tert*-butyl radical from an earlier PES study from this laboratory[20] (6.70 ± 0.03 eV) gives 12.0 ± 0.5 kcal mol^{-1} for the heat of formation of the *tert*-butyl radical, in excellent agreement with the value of 12.5 kcal mol^{-1} recently recommended by Tsang.[21] Combining these absolute values with the adiabatic ionization potential of the benzyl radical,[6] the relative chloride affinity between *tert*-butyl- and benzylcarbonium ions,[5] the heats of formation of the parent chlorocarbons,[22] and $\Delta H_f°(Cl^•)$[23] leads to a value of 88.2 ± 1.0 kcal mol^{-1} for the benzylic C–H bond energy in toluene, in excellent agreement with the value of 88 ± 1.0 kcal mol^{-1} recommended by Golden and others.[9,11-13] The heats of formation, bond energies, and hydride affinities resulting from the choice of $\Delta H_f°[(CH_3)_3C^+] = 166.5$ kcal mol^{-1} are summarized in Table I. The consistency of these data lends strong support to Tsang's recommended value of 12.5 kcal mol^{-1} for the heat of formation of *tert*-butyl radical and suggests that the value preferred by Golden[9] in a recent review may be too low. Most important, Golden's recommended values for the heats of formation of the *tert*-butyl and benzyl radicals are not consistent with current ion-thermochemistry data. If the heat of formation of *tert*-butyl radical is indeed lower than 12.5 kcal mol^{-1}, then the heat of formation of the benzyl radical must be lower by the same amount.

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Registry No. *t*-BuH, 75-28-5; *t*-$Bu^•$, 1605-73-8; *t*-Bu^+, 14804-25-2; $PhCH_3$, 108-88-3; $PhCH_2^•$, 2154-56-5; $PhCH_2^+$, 6711-19-9; *o*-$CH_3C_6H_4CH_3$, 95-47-6; *o*-$CH_3C_6H_4CH_2^•$, 2348-48-3; *o*-$CH_3C_6H_4CH_2^+$, 63246-55-9; *m*-$CH_3C_6H_4CH_3$, 108-38-3; *m*-$CH_3C_6H_4CH_2^•$, 2348-47-2; *m*-$CH_3C_6H_4CH_2^+$, 60154-94-1; *p*-$CH_3C_1H_4CH_3$, 106-42-3; *p*-$CH_3C_6H_4CH_2^•$, 2348-52-9; *p*-$CH_3C_6H_4CH_2^+$, 57669-14-4.

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